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REACTIVE ORGANIC FILLER AND ITS USE

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REACTIVE ORGANIC FILLER AND ITS USE

[Reaktiver organischer Füllstoff sowie dessen Verwendung]

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The invention concerns new reactive organic fillers in the form of a solid powder for polymerizable compositions that contain as binders compounds with radically polymerizable, ethylenically unsaturated groups. Such compositions find use in various technical fields; they have gained particular importance as dental materials. Dental materials are understood to be, for example, tooth filling compounds for conserving dental treatment and materials for making dentures or dental parts.

The incorporation of various kinds of fillers into a matrix of polymerizable monomers is already known. On the one hand, this is intended to produce a thickening, which leads to the composition having consistency that allows it to be handled before the polymerization period. On the other hand, the addition of filler is intended to improve the properties of the polymerized material, especially its hardness and compressive strength, and to reduce its tendency to shrink.

Inorganic fillers having various chemical compositions are widely used. However, since inorganic fillers in general provide only a poor bond with an organic matrix, the mechanical properties of the polymers initially were not satisfactory. To improve the bond the inorganic fillers are superficially treated with a silane. However, such silanized inorganic fillers also do not satisfy all of the requirements made on them completely.

The use of organic bead polymers, which can optionally in turn contain inorganic fillers, is also known. Such bead polymers are preferably synthesized from the same monomers that serve as binder in order to achieve compatibility that is as high as possible. For example, bead polymers of polymethylene methacrylate or other radically polymerized acrylates are known, see DE-OS 28 60 918 and EP-OS 23 321. It is difficult to control the radical polymerization, and there always remains behind a portion of unreacted monomers. Also, such fillers in general do not become sufficiently anchored in the matrix. Fillers with average diameter greater than 1 μm give a dental material the disadvantageous property that after hardening it cannot be sufficiently polished, and filler particles break off from it under the stress of chewing, which also accelerates the wearing down of the matrix polymer. These problems are seen both with silanized coarse-particle inorganic fillers as well as with bead polymers that are filled with silanized inorganic fillers.

Thus, the problem is that the bond between filler and matrix is too weak with the known inorganic and organic fillers. Up to now the modification of the filler so that the bond with the polymerized matrix is really satisfactory in every regard has not been successful. All greater modifications in the composition or preparation of the filler have at the same time led to major changes in the physical properties, so that the use of the filler as a solid filler is no longer a possibility.

The invention is based on the task of developing an organic filler that provides a solid bond between the filler and the matrix because of a high content of reactive groups that are copolymerizable with the matrix monomers and thus, after polymerization, produces materials that have considerably better cracking resistance, stress resistance and wear resistance.

The object of the invention is a reactive organic filler in the form of a solid powder, which is characterized by the fact that it is prepared by a reaction that is not radically initiated and it has at least 0.5 mmol reactive double bonds that are not extractable with solvents (determined by the DSC method), per gram of organic filler.

When the filler in accordance with the invention is used in polymerizable compositions that contain as binders compounds with radically copolymerizable, ethylenically unsaturated groups, its relatively high content of reactive double bonds leads to a solid bond between filler and matrix that has not been achieved up to now, as shown by tests of the polymerized materials: in a fatigue test they survive many times the number of load cycles of traditional materials,

which at most show the formation of cracks after ten cycles. Moreover, electron microscope investigation (SEM) of the cracking pattern shows that, with traditional materials the cracks run along the boundary lines between the matrix and filler particles, while with the materials made in accordance with the invention the bond between filler and matrix is so strong that the cracks run in a straight line along the indentation line, thus through the matrix and filler particles.

Preferably, the content of double bonds in the filler in accordance with the invention is 0.5 to 5.0, especially 1.0 to 3.0, and especially preferably 1.4 to 2.6 mmol/g of the organic filler. This high content of reactive double bonds is achieved by the fact that the filler is polymerized by a nonradically initiated reaction, preferably an addition reaction, so that 75 to 95% of the ethylenic double bonds contained in the monomers that are used are also still present in the filler powder. With the traditional synthesis of bead polymers by radical polymerization, in contrast, most of the double bonds are consumed by the polymerization reaction. Since in accordance with the invention the monomers are reacted with each other in a stoichiometric ratio, the filler contains practically no unreacted monomers, which can be seen in the fact that the content of double bonds cannot be reduced by solvent extraction. In this way the fillers are harder than the ones that still contain monomers.

The reactive double bonds contained in the organic filler can be quantitatively determined by the DSC method (differential scanning calorimetry). For this a precisely weighed sample of the filler is mixed with a specific amount of a standardized peroxide solution, after which the solvent is carefully evaporated out. A precisely weighed amount of the filler coated with peroxide is heated in a type DSC-2 Perkin-Elmer apparatus, and the amount of heat released by the exothermic reaction that takes place is determined from the thermogram. The degree of polymerization can be determined exactly by comparison with the values for the heat of polymerization of the monomers that were used. The expression "reactive double bond of the filler" that is used in this document is meant in this sense.

Preferably, the filler in accordance with the invention is prepared by reacting (meth)acrylates that contain hydroxy groups with isocyanates in the ratio of OH groups to NCO groups of about 1:1, where at least one of the starting compounds is trifunctional or more highly functional, in order to achieve the degree of cross-linking that is sufficient to produce a solid powder. According to an especially favorable embodiment one starts with triisocyanate or polyisocyanate, where it is then also possible to use a stoichiometric deficiency of hydroxy(meth)acrylate and to achieve the necessary cross-linking with water and/or a polyol, for example an aliphatic triol, which reacts with the unreacted isocyanate groups with the formation of urea or urethane groups. On the other hand, one can also react a (meth)acrylate that has three or more hydroxy groups with a diisocyanate.

Examples of suitable hydroxy-functional (meth)acrylates are hydroxyethyl methacrylate (HEMA), polyethylene glycol methacrylate 2-hydroxy- and 2,3-dihydroxypropyl methacrylate, pentaerythritol triacrylate, and reaction products of glycidyl methacrylate with polyols, for example trimethylol propane, or carboxylic acids, for example succinic acid. Bis-GMA (bisphenol A-glycidyl methacrylate) is especially preferred.

Preferred isocyanates are aliphatic compounds like 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate, trimethylhexamethylene diisocyanate and the triisocyanate tris(6-isocyanatohexyl)biuret (Desmodur N 100, Bayer AG).

The reaction between the hydroxy(meth)acrylates and isocyanates can be carried out under mild conditions. The temperature is a maximum of about 150°C, preferably about 10 to 60°C. A catalyst can be added in order to accelerate the reaction; tertiary amines and organometal salts are suitable in particular.

The reaction of hydroxyl-functional (meth)acrylates as such is already known. This reaction serves, for example, for a preparation of prepolymers, which can be used as binders in dental material, see DE-OS 21 26 419.

The filler in accordance with the invention can also be prepared by ionic copolymerization of hydroxy(meth)acrylates with an epoxy resin and/or trioxane in a stoichiometric ratio. For example, bisphenol A diglycidyl ether (Epikote 828) can be reacted with glycidyl methacrylate and/or HEMA using BF_3 as catalyst. Similar results are produced by the reaction of glycidyl (meth)acrylate with trioxane and of epoxides with epoxy(meth)acrylates. Other examples are the reaction of hydroxy compounds with carboxylic acid derivatives to form polyesters, where at least one of the starting compounds contains (meth)acrylate groups, and the reaction of allylidenes, for diallylidene pentaerythritol, with alcohols or carboxylic acids. The ethylenically unsaturated groups remain unchanged in these reactions as well and are available as reactive groups for the subsequent reaction with the matrix binder.

After its synthesis, the filler in accordance with the invention is brought to the required particle size by grinding. Preferably, the average particle size of the ground filler lies in the range from 0.5 to 100 μm . An average particle size of about 10 to 50 μm is particularly favorable.

According to an advantageous embodiment of the invention an inorganic and/or nonreactive organic filler is incorporated into the reactive organic filler, which advantageously takes place by adding the filler to the starting compounds before the addition reaction. The physical properties of the filler can additionally be varied in wide limits. The content of inert fillers in the reactive filler can be between 0 and 80 wt%, with respect to the total weight of the filler. Contents from 20 to 75, especially from about 40 to 70 wt%, are especially advantageous.

A large number of inorganic compounds are suitable as fillers. Examples are glass powders, aluminum oxide, silicon dioxide such as quartz, sand or silica, diatomaceous earth,

calcium carbonate, clay, talc, pumice, ground slag, mica, asbestos, aluminum sulfate, calcium sulfate, or lithopone. Also suitable are molybdenum sulfide, graphite, carbon black, flyash, potassium titanate or even fibers, for example glass fibers or carbon fibers. If the filler is used in dental materials glass powders or quartz powders as well as finely divided silicic acids, especially microfine pyrogenic, and also precipitated silicic acids, are especially suitable. Another preferred groups consists of inorganic fillers, which make the ready to use dental material x-ray-opaque, for instance barium sulfate or fluorides of rare earth metals.

For many applications the inorganic filler is preferably superficially silanized, in order to facilitate its incorporation into the organic materials and, if silanes with polymerizable double bonds are used, to achieve a certain bond between the organic matrix and the inorganic filler. An especially preferred silane is γ -methacryloxypropyltrimethoxysilane. Other suitable silanes are the ones with hydroxy, amino and epoxide groups.

In the synthesis of the filler in accordance with the invention it is important to keep in mind that the optionally added inorganic filler can contain groups on its surface that participate in the reaction; for example silicic acids have superficial silanol groups SiOH , which are capable of reacting with isocyanate groups. The content of such OH groups in the inorganic filler therefore must be taken into account in establishing the OH:NCO ratio of the starting compounds.

Suitable inert organic filler are in particular acrylic and methacrylic polymers, for example polymethyl methacrylate, and polyurethanes. These polymers are brought to the desired particle size by grinding.

Another object of the invention is the use of the reactive organic fillers described above in more detail in polymerizable compositions that contain as binders compounds with radically polymerizable ethylenically unsaturated groups. Suitable vinyl compounds for such compositions with the reactive organic filler in accordance with the invention are, among others, 4-methacryloxyethyltrimellitic acid and its anhydride, epoxy acrylates of bisphenol type and their oligomers, urethane dimethacrylate, methyl acrylate, methyl, ethyl and butyl methacrylate; polyethylene glycol dimethacrylate, 2,2-bis(4-methacryloxypropoxyphenyl)propane, 2,2-bis(4-methacryloxypropoxyphenyl)propane, acrylonitrile, vinyl acetate, 2-cyanoacrylic acid, styrene, divinylbenzene and mixtures of these monomers. The binder can also be prepolymers or polymers that contain vinyl groups.

The fillers are especially suitable for use in radically polymerizable, especially light-hardening dental materials that also contain vinyl compounds as binders. Especially suitable for this are monofunctional or polyfunctional methacrylates, which can be used by themselves or in mixtures. Possibilities as examples of these compounds are methyl, isobutyl and cyclohexyl methacrylate, triethylene glycol dimethacrylate, diethylene glycol dimethacrylate, ethylene

glycol dimethacrylate, polyethylene glycol dimethacrylate, butanediol dimethacrylate, hexanediol dimethacrylate, decanediol dimethacrylate, dodecanediol dimethacrylate, bisphenol A dimethacrylate, trimethylolpropane trimethacrylate as well as bis-GMA and the reaction products of isocyanates, especially di- and/or triisocyanates and OH group containing methacrylates.

Examples are the reaction products of 1 mol hexamethylene diisocyanate with 2 mol 2-hydroxyethylene methacrylate, of 1 mol tris(6-isocyanatohexyl)biuret with 3 mol hydroxyethyl methacrylate, and of 1 mol trimethylhexamethylene diisocyanate with 2 mol hydroxyethyl methacrylate, which for short can be called urethane dimethacrylate. The amount of these mostly long chain compounds in the dental material varies between 10 and 50 wt%.

The following examples serve to illustrate the invention in more detail, but the invention is not limited to them.

Example 1

In a triturator a solution of 19 g hydroxyethyl methacrylate, 2.7 g water and 0.01 g dibutyltin diacetate is mixed with 20 g silanized silicon dioxide that have an average particle size of 40 nm (Aerosil OX-50, Degussa). Then 86 g tris(6-isocyanatohexyl)biuret are added to this mixture and another 88 g of the silicon dioxide filler are mixed in as homogeneously as possible. The mixture is fully homogenized on a three roll mill.

Hardening takes place in a heating chamber at 50°C over 100 h. The hard plastic is then broken up, ground in a ceramic ball mill and coarser fractions are removed by screening through a screen with mesh size of 90 µm.

The solubility is determined in a Soxhlet over 24 h with acetone and found to be 0.9%. The DSC method gives a double bond content of 1.6 mmol per gram of organic substance.

Example 2

41 g trimethylolpropane monoglycidyl methacrylate adduct and 40 g of the SiO₂ used in Example 1 (Aerosil OX-50) are mixed together in a triturator. After the addition of 69 g tris(6-isocyanatohexyl)biuret, another 70 g SiO₂ are mixed in and the resulting paste is homogenized on the three roll mill. After storage of 140 h at room temperature the resulting plastic is broken up, ground in a ceramic ball mill and screened through a 90 µm screen.

The solubility is 2.0%. DSC gave a value of 1.4 mmol double bonds per gram of organic substance.

Example 3

Example 2 was followed. Instead of trimethylolpropane monoglycidyl methacrylate, 50 g trimethylolpropane diglycidyl methacrylate were used. Then 70 g tris(6-isocyanatohexyl)biuret

and 118 g SiO₂ as in Example 1 (Aerosil OX-50), which had been silanized with 10 [g] γ -methacryloxypropyltrimethoxysilane, were added.

The solubility was 1.1% and the double bond content is 1.7 mmol per gram of organic substance.

Example 4

In a modification of Example 2, 31 g 2,3-dihydroxypropyl methacrylate, 69 g tris(6-isocyanatohexyl)biuret and 100 g silanized filler as in Example 1 (Aerosil OX-50) are homogenized on the three roll mill.

The solubility is 0.8% and the double bond content is 1.9 mmol per gram of organic substance.

Example 5

In a modification of Example 2, 75 g succinic acid diglycidyl methacrylate, 60 g tris(6-isocyanatohexyl)biuret and 144 g silanized silicon dioxide (Aerosil OX-50) are homogenized on the three roll mill.

The solubility is 2.0% and the double bond content is 2.0 mmol per gram of organic substance.

Example 6

All three components, namely 86 g tris(6-isocyanatohexyl)biuret, 121 g silanized silicon dioxide (Aerosil OX-50) and a mixture of 19 g hydroxyethyl methacrylate and 14 g trimethylolpropane, are heated to 50°C and then kneaded to a paste. A solution of 1 g hydroxyethyl methacrylate and 0.12 g dibutyltin diacetate is added and the entire mixture is completely homogenized on the three roller mill.

The solubility is 1.7% and the double bond fraction is 1.7 mmol per gram of organic substance.

Example 7

41 g bisphenol A-glycidyl methacrylate and 29 g tris(6-isocyanatohexyl)biuret are put into an LUK 025 universal laboratory kneading machine (Werner & Pfeedler, BRD) and 130 g silanized silicon dioxide (Aerosil OS-50) are kneaded in. The resulting paste is allowed to harden at 60°C for 80 h, then the plastic is broken up and ground in a ceramic ball mill for 30 h. After screening through a 90 μ m screen one obtains a powder with an average particle size of 31 μ m.

The solubility in acetone is 1.8% and the double bond fraction (by DSC) is 2.6 mmol/g organic substance.

Example 8

In a modification of Example 7, only 40% silicon dioxide is used instead of 65%. The ratio of bisphenol A glycidyl methacrylate to tris(6-isocyanatohexyl)biuret remains the same.

The solubility in acetone is 2.3% and the double bond fraction is 2.2 mmol per gram of organic substance.

Example 9

59 g bisphenol A glycidyl methacrylate and 41 g tris(6-isocyanatohexyl)biuret are homogeneously mixed in a vessel by stirring. After a hardening time of 70 h at 50°C the filler is ground and screened through a 90 µm screen.

The particle size is an average of 42.5 µm. The solubility is 2.0% and the double bond fraction is 1.7 mmol/g.

Example 10

In a modification of Example 7, 37 g silanized silicone dioxide with average primary particle size of 16 nm and BET surface of $110 \pm 20 \text{ m}^2/\text{g}$ (Aerosil R972, Nippon Aerosil Co., Ltd.) are used.

The content of double bonds is 2.1 mmol/g of organic substance.

Example 11

100 g trimethylolpropane triglycidyl methacrylate, 172 g 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate and 181 g silanized silicon dioxide are homogeneously mixed together in a vessel as in Example 1. After the addition of 0.1% dibutyltin diacetate the filler hardens over 70 h and is then ground and screened.

The double bond fraction is 1.5 mmol/g of organic substance.

Example 12 (Comparative Example) (radically polymerized filler)

An equivalent weight of silanized silicon dioxide as in Example 1 is incorporated into a solution of 79% (W) 2,2,4-trimethylhexamethylenebis(2-carbamoyloxyethyl)dimethacrylate, 20% (W) decanediol-1,10-dimethacrylate and 2% (W) benzoyl peroxide in a kneading machine. The mixture is polymerized for 24 h at 120°C. The polymer is then broken up and ground in a ball mill for 60 h. The average particle size of the filler obtained after screening is between 30 and 40 µm.

The double bond fraction is <0.5 mmol/g organic substance and the solubility is 3.1% (W).

Example 13

52.6 g of a monomer mixture with the following composition were put into a laboratory kneader:

- 84.21% 2,2,4-trimethylhexamethylenebis(2-carbamoyloxyethyl) dimethacrylate (RM-3)
- 15.00% decanediol dimethacrylate (D₃MA)
- 0.285% DL-camphorquinone
- 0.49% cyanoethylmethylaniline (CEMA)
- 0.03% 2,6-di-tert-butyl-p-cresol (BHT).

122.8 g of the filler in accordance with the invention as in Example 7 and 24.4 g silanized silicon dioxide (Aerosil OX-50) are kneaded into the mixture so that a packable paste results.

The paste is put into a metal mold (4 mm x 4 mm x 20 mm) and exposed from two sides for 90 sec using a light polymerization apparatus. The test piece, removed from the mold, is sanded with 1000 grit sandpaper, polished with aluminum oxide and stored for one week in water at room temperature.

The test piece is subjected to a fatigue test. A Wolpert/Amsler type 2TZM 771 20 KN testing machine is used as the test apparatus.

In the test a steel ball 2 mm in diameter is pressed against the surface that is in a planoparallel position to the base surface and then the pressure is relieved. The force range for such a cycle lies between 300 N during load and 50 N during unloading. The rate is 100 mm/min. The number of cycles in which the material remains undamaged is determined, i.e., no cracks appear around the indentation margin that are visible with the light microscope at 100X magnification.

With the material described above cracks first appear after 5000 cycles. The cracking pattern shows cracking in a straight line, which allows the conclusion that there is a good bond between the filler grains and the matrix, since the fracture goes through the grains and not along them. This homogeneous fracture behavior confirms that the filler made in accordance with the invention contains enough double bonds to enter into a firm bond with the matrix.

Example 14

In a departure from Example 13, the monomer mixture contains 15% RM-3 instead of 84.21%, with the remainder being replaced by bisphenol A-glycidyl methacrylate (bis-GMA). The paste is composed as follows:

- 24.36% monomer mixture
- 33.30% filler as in Example 7
- 42.34% silanized silicon dioxide (Aerosil OX-50)

In the fatigue test the test piece withstood 2000 cycles. The cracking pattern is comparable to that of Example 13.

Example 15

Another paste is prepared as in Example 13 with the following composition:

27.5% monomer mixture as in Example 14

27.5% silanized silicon dioxide (Aerosil OX-50)

45.0% as in Example 3.

The first cracks appear after 100 cycles, with a straight line crack through the filler grains.

Example 16 (Comparative Example)

The paste is prepared by analogy with Example 14. However, instead of the filler from Example 7, the filler from Comparative Example 12 is used.

In the fatigue test cracks appear after only 10 cycles. The cracks run chiefly along the filler/matrix phase boundary, so that jagged cracking lines appear. This cracking pattern shows the insufficient bond between filler and matrix clearly.

Example 17

The following pastes are prepared:

	① Aktivator- Paste	② Base- Paste
③ - Bis-GMA	28,96 %	29,09 %
④ - Triethylenglycol-dimethacrylat	10,0 %	10,0 %
⑤ - Benzoylperoxid (BPO 50%ige Paste)	0,8 %	---
⑥ - N,N-Diethanol-p-toluidin	---	0,7 %
⑦ - 2,6-Di-tert.-butyl-p-Kresol	0,04 %	0,01 %
⑧ - Übliche UV-Stabilisatoren und optische Aufheller	0,2 %	0,2 %
⑨ - Siliciumdioxid (AEROSIL OX-50)	19,9 %	19,9 %
⑩ - Füller aus Beispiel 2	40,0 %	40,0 %
⑪ - Farbpigmente und Titanoxid	0,1 %	0,1 %
	100,00 %	100,00 % G

Key: 1 Activator paste
 2 Base paste
 3 Bis-GMA

- 4 Triethylene glycol dimethacrylate
- 5 Benzoyl peroxide (BPO 50% paste)
- 6 N,N-diethanol-p-toluidine
- 7 2,6-di-tert-butyl-p-cresol
- 8 Conventional UV stabilizers and optical brighteners
- 9 Silicon dioxide (Aerosil OX-50)
- 10 Filler from Example 2
- 11 Dye pigments and titanium dioxide

The solid substances (BPO, di-tert-butyl-p-cresol, N,N-diethanol-p-toluidine, UV stabilizers and optical brighteners) are completely dissolved in the relevant monomer mixture. The pastes are prepared in a kneading machine, incorporating the fillers (silanized silicon dioxide, filler from Example 2) and the dye pigments homogeneously into the corresponding monomer solution.

The resulting pastes have an acceptable consistency and are easy to mix. The processing time after the start of mixing is 2-3 min.

The material is polymerized over 1 h at 37°C. Otherwise the testing is carried out as in Example 14.

Cracks appear after 1000 loading cycles and run in a straight line along the indentation site, which indicates good bond between the filler and the matrix.

Example 18

The following paste is prepared:

2,2,4-trimethylhexamethylenebis(2-carbamoyloxyethyl)dimethacrylate

Butanediol-1,4-dimethacrylate

Dibenzoyl peroxide

Di-tert-butyl-p-cresol

Silicon dioxide (Aerosil R972)

Filler from Example 1

Dye pigments

The paste is prepared as described in Example 17. A solid, easily processed compound, which is suitable for making dentures, as inlay material or as blending plastic for crowns and bridge work, is formed.

The polymerization of the test pieces for the fatigue is carried out in a compression polymerization apparatus (Ivomat) at 120°C and 6 bar over 10 min. Testing takes place as in Example 13. The first straight line cracks appear after 100 loading cycles.

Claims

1. A reactive organic filler in the form of a solid powder, which is characterized by the fact that it is synthesized by a nonradically initiated reaction and has reactive double bonds that are not extracted with solvent (determined by the DSC method) in an amount of at least 0.5 mmol/g of the organic filler.
2. A filler as in Claim 1, which is characterized by the fact that it is synthesized by the reaction of (meth)acrylates containing hydroxy groups with isocyanates in a ratio of OH groups to NCO groups of about 1:1, where one or more of the starting compounds is at least trifunctional.
3. A filler as in Claim 2, which is characterized by the fact that it is synthesized using a triisocyanate.
4. A filler as in Claim 2, which is characterized by the fact that it is synthesized by the reaction of a (meth)acrylate of a triol or polyol with a diisocyanate.
5. A filler as in Claim 3, which is characterized by the fact that it is synthesized using a stoichiometric deficiency of hydroxy(meth)acrylate and is cross-linked by means of water and/or an aliphatic polyol.
6. A filler as in one of Claims 2-5, which is characterized by the fact that it is synthesized from aliphatic isocyanates.
7. A filler as in Claim 1, which is characterized by the fact that it is synthesized by ionic copolymerization of (meth)acrylates that contain hydroxy groups with an epoxy resin and/or trioxane in an essentially stoichiometric ratio.
8. A filler as in one of Claims 1-7, which is characterized by the fact that it has an average particle size from 0.5-100 μm .
9. A filler as in one of Claims 1-8, which is characterized by the fact that, with respect to the total weight, it contains up to 80 wt% inorganic and/or nonreactive organic fillers, which are incorporated into the reactive organic filler by addition before polymerization.
10. A filler as in Claim 9, which is characterized by the fact that the fraction of surface groups of the inorganic filler that react with NCO and/or epoxide groups is taken into account in establishing the stoichiometric ratio of the starting compounds.
11. The use of the filler as in Claims 1-10 in polymerizable composition that contain, as binders, monomers with radically polymerizable, ethylenically unsaturated groups.
12. A use as in Claim 11, which is characterized by the fact that the filler is added to radically polymerizable dental materials that contain vinyl compounds as binders.

European
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EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ⁴)
D,A	DE-A-2 126 419 (DENTSPLY INTERNATIONAL INC.) ---		C 08 F 2/44 C 09 C 3/08 A 61 K 6/08
A	DE-A-1 592 825 (HENKEL) -----		TECHNICAL FIELDS SEARCHED (Int. Cl. ⁴)
			C 08 F C 09 C
The present search report has been drawn up for all claims.			
Place of search The Hague		Date of completion of the search January 5, 1987	Examiner CAUWENBERG C.L.M.
CATEGORY OF CITED DOCUMENTS X: Particularly relevant if taken alone. Y: Particularly relevant if combined with another document of the same category. A: Technological background. O: Non-written disclosure. P: Intermediate document. T: Theory or principle underlying the invention. E: Earlier patent document, but published on, or after the filing date. D: Document cited in the application. L: Document cited for other reasons. &: Member of the same patent family, corresponding document.			